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Graphitization behaviour of carbon fibre-glassy carbon composites

HIDEHIKO TANAKA
National Institute for Researches in Inorganic Materials, Kurakake, Sakura-mura, Niihari-gun, Ibaraki-ken, Japan

YUTAKA KABURAGI
Musashi Instiute of Technology, Tamazutumi, Setagaya-ku, Tokyo, Japan

SHIUSHICHI KIMURA
Research Laboratory of Engineering Materials, Tokyo Institute of Technology, O-okayama, Meguroku, Tokyo, Japan

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Carbon fibre–carbon composites were fabricated by aligning PAN-based carbon fibre unidirectionally in furfuryl alcohol resin char. The graphitization behaviour was investigated by an X-ray diffraction technique and by the measurement of magnetoresistance. The time–temperature superimposition study for interlayer spacing resulted in an activation energy of 242 ± 35 kcal mol^{-1}. The kinetic study on magnetoresistance agreed with the result of X-ray measurement. The activation energy is that for the graphitization of the layer structure formed in the glassy carbon matrix of the composites. The graphitization mechanism of the layer structure is the same as that of soft carbons.

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1. Introduction

Carbon fibre reinforced composites have attracted considerable attention because of their high mechanical performance [1, 2]. Composites with matrices obtained from thermosetting resins by carbonization should have improved properties, as the handling techniques of FRP, such as wet filament winding, can be applied to them.

In the present work, the graphitization behaviour of carbon fibre–glassy carbon composites has been investigated by X-ray diffraction and by measurement of magnetoresistance. The term "glassy carbon" means the carbon matrix which is obtained by the carbonization of a thermosetting resin.

The composites should be heated to a temperature above 2000° C, where they are used in practice as rocket nozzles or re-entry nose tips [3], for example. It is important for their application to understand the influences of heat treatment. In previous work, Hishiyama *et al.* and Kimura *et al.* [4, 5] found that above 2400° C the glassy carbon matrix in the composite was graphitized and a change from a glass-like carbon to a layer structure proceeded in spite of the non-graphitizing nature of glassy carbon. This seemed to be caused by the stress accumulation at the boundary due to a shrinkage difference between the fibre and the matrix.

2. Experimental procedure

2.1. Specimens and heat treatment

The carbon fibre used was a PAN-based carbonized fibre. The carbon fibre rovings were aligned unidirectionally in the furfuryl alcohol condensate by a filament winding method to achieve a homogeneous fibre distribution. After curing of the condensate, the specimens were cut into rectangular prisms of 15 mm × 12 mm × 4 mm, and carbonized at 1000° C for one hour under an atmosphere of argon. The fibre fraction of the composite was about 50 vol%.

The heat treatments at high temperatures were carried out in a graphite resistance furnace under flowing argon gas. The temperature of the furnace was measured and controlled automatically by a two-colour pyrometer, which was connected to an electric power supply. The fluctuation of the temperature was estimated to be ± 20° C. The heat treatment temperatures of 2290, 2390, 2490 and 2590° C were selected. In this temperature range, the composites showed a remarkable degree graphitization in a previous study [5]. The specimens were positioned at the top of the furnace tube. When the required temperature was obtained, they were inserted quickly (within 10 sec) into a hot zone for a measured time interval. After the heat treatment, all of the specimens were cooled down in the furnace. About three minutes were required for cooling down by 300° C.

2.2. X-ray diffraction and magnetoresistance

X-ray diffraction patterns were measured using CuKα radiation on powdered specimens with 10% Si as an internal standard. The diffraction profiles of the (0 0 4) line were used to calculate the interlayer spacing $2\bar{d}_{004}$. The profiles were corrected for the Lorentz polarization, absorption and scattering factors.

The magnetoresistance was measured at liquid nitrogen temperature by a d.c. amplification technique [6]. The electical current was always directed along the fibre axes. To obtain information as to the preferred orientation of the crystallites, the anisotropy of the magnetoresistance was measured. The magnetoresistance as a function of magnetic field orientation was studied using two magnetic field rotation schemes, as shown in Fig. 3. In the first rotation scheme which is denoted T (transverse rotation scheme), the magnetic field H is rotated in the plane perpendicular to the fibre axis. In the second rotation scheme denoted TL (transverse-to-longitudinal rotation scheme), H is rotated in the plane parallel to the fibre axis and includes the direction of H for the maximum magnetoresistance in the T rotation scheme.

3. Results and discussion

3.1. Kinetic study of interlayer spacing

Most of the (0 0 4) diffraction profiles observed on the specimens were usually asymmetrical, having a sharp peak at a higher diffraction angle, as shown in Fig. 1. The asymmetrical profile suggests the existence of some heterogeneity in the structure; part graphitized and part ungraphitized. The profiles were separated into two peaks, a sharp peak of which was denoted component G. It was observed microscopically that the component G corresponded to diffraction from the graphitic layer structure formed partly in the glassy carbon matrix [5]. The broad low angle component is the reflection from the ungraphitized part, the carbon fibre and/or the glassy carbon matrix. The interlaying spacing $2\bar{d}_{004}$ of the component G is shown by closed marks in Fig. 2, as a function of heat treatment time on a logarithmic scale. $2\bar{d}_{004}$ decreases with prolonged heat treatment. Four isotherms of $2d_{004}$ appear to follow the same behaviour with heat treatment time. The superimposition study was then applied to the isotherms of interlayer spacing, as proposed by Fischbach [7]. The isotherms of 2290, 2490 and 2590° C have

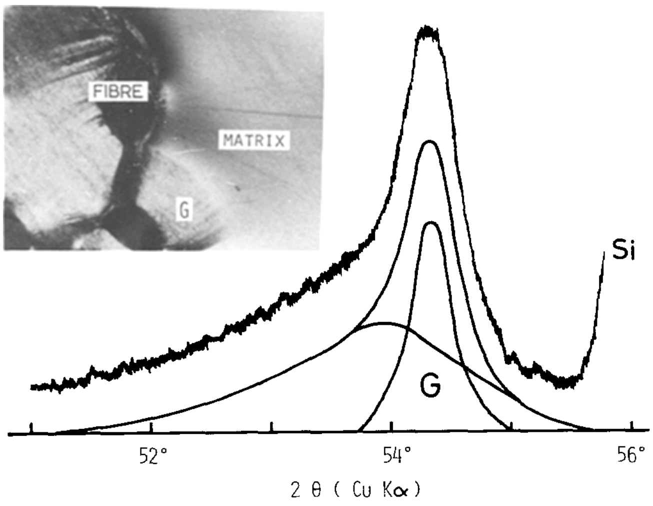

Figure 1 (0 0 4) diffraction profile and the separation of high angle component G for the specimen heat treated at 2490° C, 60 min. The inset photograph shows the structure of the composite.

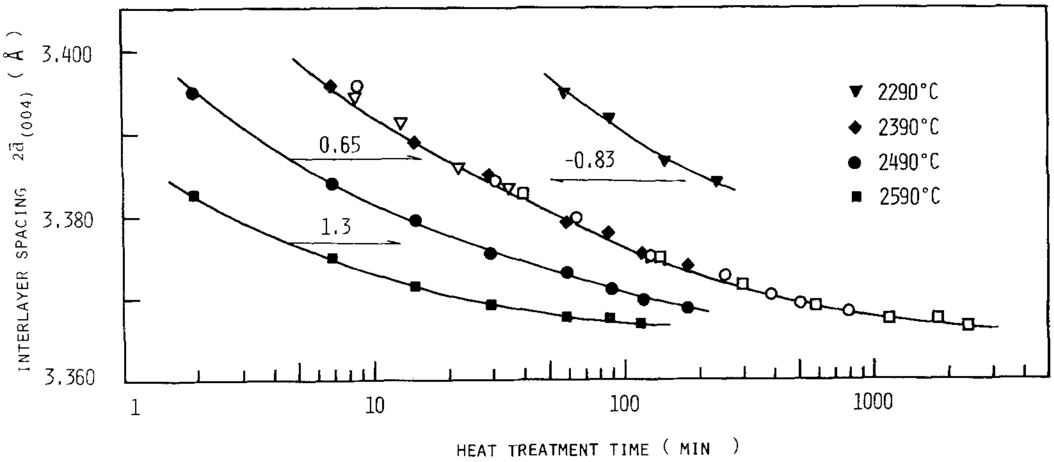

Figure 2 Change of interlayer spacing $2\bar{d}_{004}$ and superimposed master curve as a function of logarithm of time.

been shifted along the abscissa by the amount of −0.83, 0.65 and 1.3 respectively. A smooth curve for the interlayer spacing is obtained at a reference temperature of 2390° C. Arrhenius plots of the shift factors against the reciprocal temperatures yielded a value of 242 ± 35 kcal mol^{-1} as an effective activation energy.

Fischbach [7] showed that the kinetics of graphitization could be represented by a first-order rate process with a broad distribution of rate constants and a constant activation energy of about 250 kcal mol^{-1} for the temperature range 2300 to 2700° C. It was confirmed that for a wide variety of soft carbons the activation energy was about 250 kcal mol^{-1} [8, 9]. The value obtained here falls within this range, and log t versus $2d_{004}$ plots had a similar shape to those for petroleum cokes [8]. These results are perhaps related to the structural similarities between the graphitic layer structure in the glassy carbon matrix and soft carbons. It also seemed that the graphitization of the composite proceeded by the same mechanism as that of soft carbons, i.e., annealing of the defects in the layer plane [10].

3.2. Magnetoresistance and crystallite orientation

For the specimens heat treated at 2290° C and the specimen heat treated at 2390° C for 30 min, magnetoresistance, $\Delta\rho/\rho$ was negative. The value of $\Delta\rho/\rho$ changed to positive for the specimens heat treated at 2390° C for 60 min and more. Only positive magnetoresistance is considered here, because there is some theoretical ambiguity in the negative magnetoresistance. As mentioned above, the positive magnetoresistance is due to the graphite layer structure in the glassy carbon matrix.

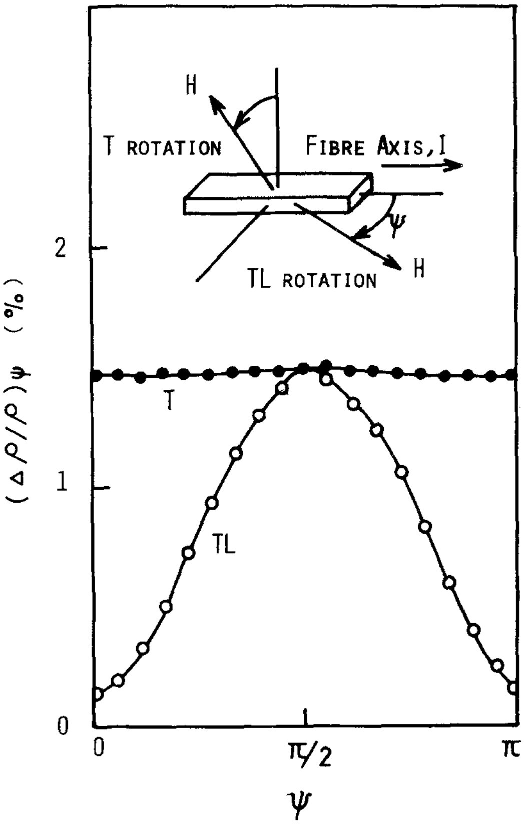

Figure 3 Dependence of magnetoresistance on the rotation angle ψ at 10 kG, 77 K for the specimen heat treated at 2390° C, 180 min.

The measured $\Delta\rho/\rho$ of the specimen heat treated at 2390° C for 180 min is shown in Fig. 3, as an example. The figure shows that the change

TABLE I Magnetoresistance and interlayer spacing

Heat treatment		$(\Delta\rho/\rho)_{cr}$ (%)	A	$2\bar{d}_{(004)}$
Temperature (° C)	Time (min)			
2590	60	10.32	0.947	3.3678
2490	180	8.52	0.939	3.3684
2590	30	6.77	0.946	3.3695
2490	90	6.02	0.943	3.3707
2590	15	4.62	0.947	3.3719
2490	60	4.39	0.945	3.3730
2390	180	3.14	0.949	3.3742
2590	7	2.81	0.947	3.3754
2490	30	2.73	0.952	3.3753
2390	120	2.25	0.949	3.3782
2390	90	1.84	0.955	3.3782
2390	60	1.01	0.950	3.3794
2590	2	0.75	0.967	3.3833

of $\Delta\rho/\rho$ in the TL rotation scheme obeys a $\cos^2\psi$ dependence, while $\Delta\rho/\rho$ in the T rotation scheme remains almost constant at the maximum value in the TL rotation scheme. This dependence of magnetoresistance on magnetic field orientation indicates that the layers of graphite crystallites are uniaxially oriented parallel to the fibre axes.

The dependence of magnetoresistance on the rotation angle in the TL rotation scheme can be written [11]

$$(\Delta\rho/\rho)_\psi = (\Delta\rho/\rho)_{cr}[A/2 + (1-3A/2)\cos^2\psi], \quad (1)$$

where $(\Delta\rho/\rho)_\psi$ is a value observed at an angle ψ, $(\Delta\rho/\rho)_{cr}$ an average transverse magnetoresistance of crystallites, and A an anisotropy factor. The factor A changes from 0 for a single crystal to 2/3 for a random distribution, and 1 for a perfect cylindrical alignment of layer planes. $(\Delta\rho/\rho)_{cr}$ is the maximum transverse magnetoresistance to be measured when the c-axes of the crystallites are oriented parallel to each other, i.e. $A = 0$. The values of A, $(\Delta\rho/\rho)_{cr}$ and $2\bar{d}_{004}$ of the specimens studied are listed in Table I. The high values of A, about 0.95 for all the specimens investigated, show the high uniaxial orientation of the crystallites. This preferential alignment of the layers was thought to occur at the early stage

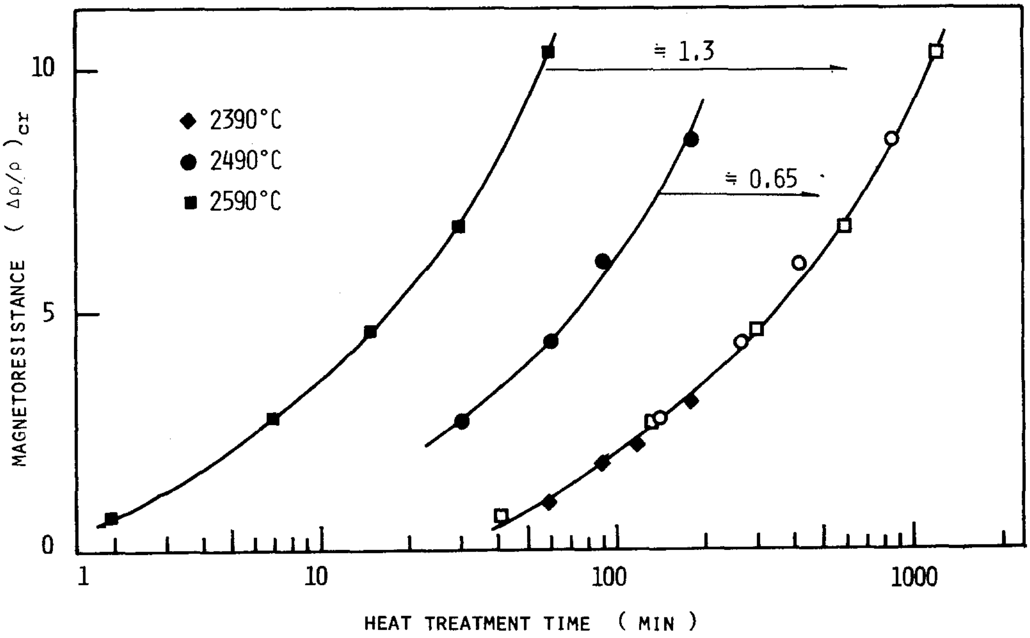

Figure 4 Change of average transverse magnetoresistance of crystallites $(\Delta\rho/\rho)_{cr}$. The experimental values of $(\Delta\rho/\rho)_{cr}$ are indicated by closed marks, and the shifted values by open marks.

of graphitization, because the specimen heat treated at 2590° C for 2 min had a high value of A, though $2\bar{d}_{004}$ was still 3.38 Å (Table I).

3.3. Kinetic study of magnetoresistance

To consider the magnetoresistance kinetically, the values of $(\Delta\rho/\rho)_{cr}$ are plotted against the logarithm of heat treatment time in Fig. 4. The isotherm of 2290° C was not obtained because the magnetoresistance was negative in the specimens treated at this temperature. The superimposition method was applied again in the same manner as in Fig. 2. The closed marks in Fig. 4 are the original values, the open marks the shifted ones. The smooth master curve of 2390° C is obtained. The effective activation energy is estimated at about 240 kcal mol^{-1}. This value corresponds to 242 ± 35 kcal mol^{-1}, which was calculated from $2\bar{d}_{004}$. It is thus confirmed that the same activation energy can be obtained by two different methods – X-ray interlayer spacing and magnetoresistance measurements.

These results for the activation energy of about 240 kcal mol^{-1} indicate that the graphitization of the composite has proceeded by the mechanism of annealing of defects in the layer planes. This mechanism is the same as that of the graphitization of soft carbons, in which the graphitization can proceed without any applied stress. Thus, in the composite, the stress does not seem to take part in the graphitization of the glassy carbon matrix. It has, however, been found that the glassy carbon could be actually graphitized only under the influence of a stress field. Kamiya *et al.* [12] showed that the glass-like carbon changed to the graphite structure under a pressure of 5 kbar at 1500° C. In this study, it should be noted that the measurements of interlayer spacing and magnetoresistance correspond to those of a graphite-like layer structure. It is concluded that there is no stress graphitization in the graphite layer structure developed in the glassy carbon matrix. The stress may play some role, if it exists in the stage of carbonization, in the change of the glassy carbon matrix to the layer structure.

4. Summary

The carbon fibre–glassy carbon composite was graphitized at temperatures above 2290° C. The graphitization behaviour was investigated by X-ray diffraction and magnetoresistance measurements. The graphitization of the composite proceeded in the layer structure formed in the glassy carbon matrix. The effective activation energy for the graphitization is about 240 kcal mol^{-1}, which suggests that the graphitization is caused by a defect annealing process. Stress graphitization was not detected by the studies of X-ray interlayer spacing and magnetoresistance.

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